

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C09K 21/08, 21/12		A1	(11) International Publication Number: WO 96/11996 (43) International Publication Date: 25 April 1996 (25.04.96)
(21) International Application Number: PCT/US95/12702		(81) Designated States: CA, JP, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).	
(22) International Filing Date: 12 October 1995 (12.10.95)		Published <i>With international search report.</i>	
(30) Priority Data: 08/322,879 13 October 1994 (13.10.94) US			
(71) Applicant: AKZO NOBEL NV [NL/NL]; Velperweg 76, P.O. Box 9300, NL-6800 SB Arnhem (NL).			
(71)(72) Applicants and Inventors: BRIGHT, Danielle, A. [US/US]; 21 Zabela Drive, New City, NY 10956 (US). AARONSON, Alan, M. [US/US]; 65-48 173 Street, Fresh Meadows, NY 11365-2033 (US). PIRRELLI, Ronald, L. [US/US]; 61 Oak Ridge Circle, Mahopac, NY 10541 (US).			
(74) Agent: FENNELLY, Richard, P.; Akzo Nobel Inc., 7 Livingstone Avenue, Dobbs Ferry, NY 10522 (US).			

(54) Title: VISCOSITY MODIFICATION OF HIGH VISCOSITY FLAME RETARDANTS

(57) Abstract

Alkylene-bridged diphosphate compounds can be used to modify, namely reduce, the viscosity of fluid flame retardants (polybrominated aryl oxides, oligomeric phosphate esters, etc.) which are useful in flame retarding polyurethane and thermoplastic compositions.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

**VISCOSITY MODIFICATION OF HIGH
VISCOSITY FLAME RETARDANTS**

BACKGROUND OF THE INVENTION

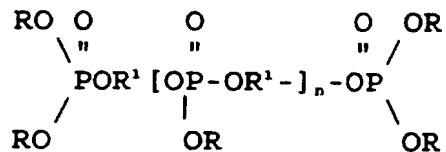
Polyurethane foams, coatings and elastomers are commonly admixed with flame retardants to achieve the desired degree of flame retardancy for the final material desired. Pumpable fluid (or liquid) flame retardant compositions are a preferred class since such pumpable formulations are needed in environments where automation and machine mixing of the various components are used. Examples of the chemical classes for such fluid or liquid flame retardants include brominated aryl flame retardants, such as polybromodiphenyl oxide, and various viscous organophosphorus flame retardants such as the oligomeric phosphate esters, such as the chlorinated oligomeric phosphate esters (e.g. FYROL 99 brand) and the reaction product of 2-chloro-1-propanol phosphate (3:1) with ethylene oxide and phosphorus pentoxide (FYROL PCF brand), and the aromatic oligomeric phosphate esters such as those containing an arylene bridging group derived from a diol such as bisphenol A, hydroquinone or resorcinol.

High viscosity in such fluid or liquid flame retardant compositions can be disadvantageous since it makes the pumping and movement of such compositions more difficult thereby complicating manufacturing operations. It can also hinder the flow of thermoplastic polymers containing such a viscous flame retardant. For example, it is known that polybrominated diphenyl oxide flame retardants are very viscous. U.S. Patent No. 4,746,682 to J. Green indicates that either alkyl diphenyl phosphates or alkylated triaryl phosphates can be used to achieve blends having acceptably low viscosity as compared to the polybrominated aryl flame retardant itself. Copending U.S. Serial No. 215,406, filed March 14, 1994, describes the use of triphenyl phosphate as a viscosity reduction additive for viscous flame retardants. However, the relatively low volatility of the triaryl phosphates makes them unsuitable for certain applications where high processing temperatures may cause juicing.

SUMMARY OF THE INVENTION

It has now been found that an alkylene-bridged diphosphate compound is an effective viscosity modifying, namely, reducing agent in the aforementioned types of liquid, but viscous, flame retardant compositions. This type of material is less volatile than a triaryl phosphate compound. It also has a higher phosphorus content resulting in an increased flame retardancy efficacy as compared to a triaryl phosphate compound.

10 The terminology "alkylene-bridged diphosphate compound" is to be understood to encompass monomeric and low oligomeric species of the formula



Where R is aryl, such as unsubstituted phenyl, n is a number ranging from 0 to about 5, and R' is alkylene of from 1 to 8 carbon atoms.

20 The level of use of the diphosphate viscosity modification additive of the present invention with a particular flame retardant will depend upon its initial compatibility or miscibility with the flame retardant component whose viscosity is initially high and in need of reduction. The level of diphosphate to use is also
25 dependent upon the ultimate viscosity that is desired for the composition containing it. Generally, the amount of diphosphate that needs to be added will range from about 5% to about 80%, by weight of the fluid or liquid flame retardant whose viscosity is to be reduced, preferably from about 5% to about 50%, more preferably
30 from about 5% to about 30%.

The liquid flame retardants to which the instant invention can be added include polybrominated diphenyl oxide and aromatic oligomeric phosphates (e.g., resorcinol bis(diphenyl phosphate), bisphenol A bis(diphenyl phosphate), poly(resorcinol phenylphosphate), and the like.

The aromatic bisphosphates to which the above-described alkylene-bridged diphosphate species can be added are of the same formula given above with the exception that R' is derived from an arylene diol, such as resorcinol, bisphenol A, or hydroquinone, and n is generally from 0 to about 15. The diphosphate viscosity reducing additive of the instant invention can also be used in similar amount with flame retardant compositions which contain oligomeric phosphate esters as the sole or predominant component. Generally speaking, it has been found that up to about 50%, by weight of the alkylene-bridged diphosphate compound, based on the weight of the entire composition, can be used in such systems.

The instant invention allows for the obtaining of low enough viscosities to achieve pumpable flame retardant compositions which are required to satisfactorily process flexible and rigid polyurethane foams, for example. Easier machine mixing and miscibility are achieved by bringing the viscosities of the components closer and preferably lower. Coatings and elastomers also require low viscosities for better flowability and processing.

The present invention is illustrated by the Examples which follow.

EXAMPLES 1-19

A series of compositions were tested in regard to their viscosity at 23°C ± 0.5°C. in a Brookfield viscometer. The Table given below shows the results which were obtained.

5 (The viscosity of the additives responsible for viscosity reduction were as follows: neopentyl glycol bis(diphenyl-phosphate) - 549; ethylene glycol bis(diphenylphosphate) - 319; and propylene glycol bis(diphenylphosphate) - 367.5.

10

TABLE

	<u>Composition - Amount (wt %)</u>		<u>Viscosity (cps)</u>
	Bisphenol A bis(diphenyl phosphate)	100%	20,900
	Bisphenol A bis(diphenylphosphate)	90%	
	Neopentyl glycol bis(diphenylphosphate)	10%	12,000
15	Bisphenol A bis(diphenylphosphate)	80%	
	Neopentyl glycol bis(diphenylphosphate)	20%	8,292
	Bisphenol A bis(diphenylphosphate)	50%	
	Neopentyl glycol bis(diphenylphosphate)	50%	2,616
	Bisphenol A bis(diphenylphosphate)	90%	
20	Ethylene glycol bis(diphenylphosphate)	10%	11,700
	Bisphenol A bis(diphenylphosphate)	80%	
	Ethylene glycol bis(diphenylphosphate)	20%	6,548
	Bisphenol A bis(diphenylphosphate)	50%	
	Ethylene glycol bis(diphenylphosphate)	50%	1,752
25	Bisphenol A bis(diphenylphosphate)	80%	
	Propylene glycol bis(diphenylphosphate)	20%	7,380
	Bisphenol A bis(diphenylphosphate)	50%	
	Propylene glycol bis(diphenylphosphate)	50%	2,052
	Resorcinol bis(diphenyl phosphate)	100%	691

	Resorcinol A bis(diphenylphosphate)	90%	
	Neopentyl glycol bis(diphenylphosphate)	10%	670.5
	Resorcinol A bis(diphenylphosphate)	90%	
	Ethylene glycol bis(diphenylphosphate)	10%	636
5	Resorcinol A bis(diphenylphosphate)	90%	
	Propylene glycol bis(diphenylphosphate)	10%	666
	Pentabromo Diphenyloxide	70%	
	Neopentyl glycol bis(diphenylphosphate)	30%	8,670
0	Pentabromo Diphenyloxide	50%	
	Neopentyl glycol bis(diphenylphosphate)	50%	2,090
	Pentabromo Diphenyloxide	70%	
	Ethylene glycol bis(diphenylphosphate)	30%	5,090
	Pentabromo Diphenyloxide	50%	
	Ethylene glycol bis(diphenylphosphate)	50%	1,225
5	Pentabromo Diphenyloxide	70%	
	Propylene glycol bis(diphenylphosphate)	30%	5,590
	Pentabromo Diphenyloxide	50%	
	Propylene glycol bis(diphenylphosphate)	50%	1,395

The foregoing data is presented for purposes of illustrating certain embodiments of the present invention and, for that reason, should not be construed in a limiting sense. The scope of protection sought is set forth in the claims which follow.

We Claim:

1. A fluid flame retardant composition suitable for use in forming flame retarded polymer composition which comprises a normally viscous flame retardant and an effective amount of an alkylene-bridged diphosphate compound for viscosity modification thereof.

2. A composition as claimed in Claim 1 wherein the flame retardant composition comprises a major amount of a polybrominated diphenyl oxide.

10 3. A composition as claimed in Claim 2 wherein the flame retardant is pentabromodiphenyl oxide.

4. A composition as claimed in Claim 1 wherein the flame retardant composition comprises a major amount of an aromatic oligomeric phosphate ester flame retardant.

15 5. A composition as claimed in Claim 1 wherein flame retardant composition comprises a major amount of a high molecular weight chloroalkyl phosphate.

20 6. A composition as claimed in Claim 1 wherein the alkylene-bridged diphosphate is present at up to about 50%, by weight of the entire composition.

7. A composition as claimed in Claim 2 wherein the alkylene-bridged diphosphate is present at up to about 50%, by weight of the entire composition.

25 8. A composition as claimed in Claim 4 wherein the alkylene-bridged diphosphate compound is present at up to about 50%, by weight of the entire composition.

9. A composition as claimed in Claim 5 wherein the alkylene-bridged diphosphate compound is present at up to about 50%, by weight of the entire composition.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US95/12702

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C09K 21/08, 21/12

US CL : 252/609

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 252/609, 601, 602, 603, 604, 605, 606, 607, 608; 521/107; 558/164

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
NONEElectronic data base consulted during the international search (name of data base and, where practicable, search terms used)
APS, STN/CAS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US, A, 4,433,071 (FESMAN) 21 February 1984, see abstract, and column 1, line 64 to column 3, line 17.	1-9
Y	US, A, 4,565,833 (BUSZARD ET AL.) 21 January 1986, see abstract, and column 2, lines 52-68.	1-9
Y	US, A, 4,681,902 (DUNCAN ET AL.) 21 July 1987, see abstract, column 1, line 48 to column 2, line 34, and Example 1.	1-9
Y	JP, A, 49-40342 (ASAHI DENKA KOGYO K.K.) 15 April 1974, see English translation, page 1 and page 8, lines 7-11.	1-9
X	US, A, 5,086,082 (STONE) 04 February 1992, see abstract, and column 3, lines 20-30.	1-3, 6-7

 Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T"

later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X"

document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y"

document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"Z"

document member of the same patent family

Date of the actual completion of the international search

05 JANUARY 1996

Date of mailing of the international search report

22 JAN 1996

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Authorized officer

JOSEPH D. ANTHONY

Facsimile No. (703) 305-3230

Telephone No. (703) 308-1235

